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<p>(21) International Application Number: PCT/US93/01812 (22) International Filing Date: 3 March 1993 (03.03.93) (30) Priority data: 07/845,129 3 March 1992 (03.03.92) US (71) Applicant: EXXON CHEMICAL PATENTS, INC. [US/US]; 5200 Bayway Drive, Baytown, TX 77520-5200 (US). (72) Inventors: OHLSSON, Stefan, Bertil ; Montagne au Chaudron 6, Box 4, B-1150 Brussels (BE). WILLEMS, William, Frans, Maria, Josef ; Sparrenweg 12, B-3140 Keerbergen (BE). ROHSE, Norbert ; Nederlandlaan 30, B-3090 Overijse (BE). LAMBERT, Philippe, Marie ; 805 Greenleaf, Wilmette, IL 60091 (US). PATRICK, William, David ; 3201 Jasmine Court, Crystal Lake, IL 60012 (US).</p>		<p>(74) Agents: MULCAHY, Robert, W. et al.; Exxon Chemical Company, P.O. Box 2149, Baytown, TX 77522-2149 (US). (81) Designated States: European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: STERILIZABLE HEAT-SEALED CONTAINERS OF HIGH ETHYLENE RANDOM COPOLYMER FILMS AND PROCESSES</p> <p>(57) Abstract</p> <p>Heat-sealable containers or pouches of plastic film, which are heat-sterilizable at temperatures between about 120 °C and 130 °C and which reform their heat seals at such temperatures in order to retain the flexibility and resistance of the heat seals to rupture or leak under impact and/or compression forces. The novel pouches or containers are produced by superposing films of isotactic random reactant polymers of polypropylene containing from about 5% to about 20% by weight of ethylene, and heat sealing the films to each other to form containers or pouches on which the heat-seals remelt and reform during heat-sterilization at a temperature within the range of from about 120 °C to about 130 °C.</p>		

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STERILIZABLE HEAT-SEALED CONTAINERS OF HIGH
ETHYLENE RANDOM COPOLYMER FILMS AND PROCESSES

Background of the Invention

Field of the Invention:

5 The present invention relates to heat-sealed
containers of thermoplastic films and, more
particularly, to such containers which are
heat-sterilizable at temperatures between about
120° to 130°C, clear or transparent and resistant
10 to rupture if dropped onto a hard surface at
ordinary ambient conditions. Such containers are
commonly used in the food and medical industries.

Summary of the Prior Art:

15 It is known to produce sterilizable and retortable
heat-sealed containers or pouches from
thermoplastic films and laminates of such films,
some such containers being clear or transparent.

A retort container or pouch must possess the
following properties, all of which are provided or
20 affected by the inner seal layers:

1. they must be heat sealable for closing the
container securely following filling;

2. they must be flexible and yet have sufficient toughness and impact strength to enable the pouch to withstand severe abuse testing in accordance with industry shipping standards.

5 3. they must be capable of withstanding sterilization at temperatures in the range of 121°C to 135°C to kill botulism;

4. they must possess non-blocking properties in that the interior opposed faces of the container
10 must not stick together which would impede filling of the pouch;

5. the film used in the pouches must be processable without sticking as it is unrolled from the film roll during manufacture of the pouches and
15 subsequent sterilization;

6. they must have sufficient capacity to be economical. (Institutions serving large numbers of people are not likely to use extensively containers having capacities less than one liter).

20 Most commonly such containers or pouches are produced from thermoplastic films having melting points above about 135°C, so as to require sterilization or retort temperatures of 135°C or higher. Unless the containers or pouches are
25 heated to the softening temperature of the heat-sealed films, the heat seal does not soften and reform but rather becomes brittle when the container is cooled, whereby the container is

susceptible to rupture if dropped at ambient conditions. At retort temperatures the fluids within the heat sealed container are generally steam autoclaved at a temperature of about 121°C, and the heat-sealed film must have a low water loss at such temperature during autoclaving and storage.

The use of higher autoclave temperatures above about 130°C and up to about 160°C, as required to soften prior-known heat-sealed containers, subjects the containers to more excessive autoclave conditions which can result in higher water loss during autoclaving and increased embrittlement and susceptibility to rupture if dropped.

It is known according to Japanese Application 59-74,109 to produce retortable film pouches from films comprising blends of two different types of polypropylene polymers, one being a random copolymer of propylene and ethylene having a low ethylene content of from 0.7 to 5.3 wt%, and the other being a block copolymer having an ethylene content of 40-80%. The average ethylene content of the blend is 5.5 to 17%. The random copolymer is formed in a first step and the blend is formed in a second step. The film has a melting point of 135°-155°C, preferably 140°-150°C.

Heat sealed pouches produced according to the Japanese application require high heat-seal temperatures above the softening point of the film, i.e., above about 135°-155°C, and require similar retort temperatures in order to soften and reset

the heat seal during retort. Otherwise the heat seal becomes embrittled during retort and the container or pouch is susceptible to rupture if dropped on a hard surface at ambient temperatures.

5 It is also known according to U.S. Patents 4,857,409 and 4,769,261 to produce retortable, heat-seal pouches from film laminates which may include skin layers comprising blends of random reactor copolymers of polypropylene and from about
10 1% to 6 wt% ethylene or of impact reactor copolymers of propylene and from about 6% to 20 wt% ethylene, with elastomers such as rubbers.

Containers or pouches produced according to Patents 4,857,409 and for 4,769,261 are relatively
15 expensive, due to the tri-film construction, and are unsatisfactory for low temperature sterilization at temperatures of 125°C or less because they have higher remelt temperatures and lower strength at remelt temperatures than is
20 desirable. Thus unless they are heated to remelt temperatures of 135°C or more during retort, the heat seals are not reformed and become brittle after cooling, whereby the impact strength of the sealed container is unsatisfactory, especially for
25 container sizes of one liter or more in capacity.

Summary of the Invention

The present invention is concerned with the production of heat-sealable, soft, optically-clear containers or pouches which can be formed of

heat-sealable monofilms having high tensile strength, and which have low remelt temperatures of about 131°C or less which permit sterilization of the filled, heat-sealed containers at said
5 temperatures to reform the original heat seal of the container and preserve its original impact strength against rupture if the container is dropped onto a hard surface.

The objects and advantages of the present invention
10 are accomplished by the discovery that films of certain polypropylene copolymers, namely isotactic random reactor copolymers of propylene containing a high content of ethylene, i.e., from about 5 to about 20 wt%, have excellent properties of tensile
15 strength, clarity, non-blocking, low remelt, heat-sealability and related properties, so as to provide excellent results when formed into heat-sealable containers or pouches capable of being sterilized and seal-reformed at temperatures
20 of about 131°C or less, to preserve their impact strength against rupture if dropped. The present copolymer films have lower hot tack temperatures and therefore are heat-sealable at lower temperatures and/or in shorter time periods than
25 higher-melting films.

Description of the Drawings

FIG. 1 is a graph illustrating the comparative heat seal strengths of sterilizable pouches produced according to the prior art (Film 1) and according
30 to the present invention (Film 2), and

FIG. 2 is a graph illustrating the comparative hot tack properties of heat seals formed on pouches of Films 1 and 2.

Detailed Description

5 The novel heat-sealable, steam-sterilizable containers or pouches of the present invention contain an inner seal film consisting of an isotactic random reactant copolymer of polypropylene and from about 5% to about 20% by
10 weight of ethylene, which film has high tensile strength, good optical clarity, non-blocking and low remelt temperatures, in the area of 120°C to 130°C. The present filled containers can be heat-sealed at lower temperatures and/or under
15 shorter heat-sealing durations than prior known inner seal films having higher remelt temperatures. Most importantly the present filled, heat-sealed containers can be sterilized at lower botulism-killing temperatures, between about 121°C
20 and 131°C, while undergoing remelt and reform of the heat-seal and alleviating the necessity for higher temperatures which can result in excessive water loss during autoclaving. The remelt or reform of the heat seal, preferably at a
25 temperature of 125°C or less, causes the outline of the heat seal to change from a sharp to a rounded outline, evidencing fusion, and results in a flexible, reformed seal on cooling which is resistant to rupture under impact.

The present random reactor copolymers of polypropylene containing high amounts of ethylene may be produced by well-known polymerization methods using a Ziegler catalyst such as AlCl_3 and TiCl_4 . Such copolymers have a density between about 0.86 and 0.92 gr/cc measured at 23°C according to ASTM D 1238 (conditions of 230°C and 2.16kg).

The calculation of the ethylene content of the present random copolymers is determined by compression molding a plaque of the copolymer and measuring the height of the ethylene peak on a FTIR Spectrometer (type FTS 40-Digilab) according to test procedure P516.

In order to demonstrate the unexpectedly superior results arising from the use of the present random reactor copolymer films as inner seal films for heat-sealable flexible containers or pouches, such containers were produced according to the present invention and compared to similar containers produced according to commonly-assigned U.S. Patent 4,857,409.

The first film (Film 1 hereunder) which was for comparison purposes, is an 8 mil. ABA cast coextruded structure as described in USA patent 4,857,409; it consisted of a 6 mil. core of an elastomeric alloy consisting of a random copolymer of 97% propylene and 3% ethylene blended with polyisobutylene rubber. Then random copolymer of propylene and ethylene has a density of about 0.90

g/cc measured at 23°C according to ASTM D1505 and a melt flow index of 1.7 gr/10 min. as determined according to ASTM D1238 (conditions 230°C and 2.16 Kg). On both faces of the core, there was a 1 mil. skin film of a pure random copolymer of propylene and ethylene, as described above.

The second film (Film 2 hereunder) is an 8 mil. monolayer blown on a tubular water bath, as described in USA patents 4,203,942 and 3,872,285, for example. Film 2 is made out of a pure random copolymer of propylene and ethylene with a 6.6 ethylene weight %, and a melt flow index of 1.3 gr/10 min. as determined according to ASTM D1238 (conditions 230°C and 2.16 Kg).

The accompanying Tables 1 to 3 and Figures 1-2 show the results obtained for the tensile strength at yield and at break, the elongation at yield and at break, the secant moduls, optical, barrier and seal properties.

These tests were carried out as follows:

Tensile strength, elongation, secant modules (1½)

These mechanical resistance tests were determined with an Instron tester according to ASTM D882.

Haze

The optical properties of the film were determined with a Gardner Hazemeter, haze according to ASTM D1003.

5 Barrier Properties

Humidity barrier properties were determined by measuring the water vapor transmission rate (WVTR) according to ASTM F372 at 37.8°C and 100% relative humidity using a Permatran W5 instrument from
10 Modern Controls incorporated.

Seal Strength (packforsk)

This is the "cold" heat seal strength of the film which is measured after the seal has cooled to ambient temperature and the full potential strength
15 of the seal has developed.

A packforsk Hot Tack Tester (model 52-B) from Design & Test Consult AB (Bromme-Sweden) was used to make the heat seals. A strip of 15mm wide and some 280mm long is folded over upon itself and
20 sealed together between the heated jaws of this instrument.

The formed seal has an area of some 15 x 5 mm. Dwell conditions on the seal have been kept constant at a pressure of 10 bar and a dwell time
25 of 0.5 seconds. To measure the seal strength, the instrument is used in a mode whereby, upon opening

of the sealing jaws, the automatic peeling action used for hot tack measurements is not activated. The seal is instead cooled to ambient temperature. The unsealed ends of the strip are then attached to
5 the jaws of a tensile testing machine. The force required to break the seal at a rate of 500 mm/min. is recorded by the tensile tester and expressed as the seal strength in N/15 mm.

Hot Tack

10 This is the strength of the heat seal measured just after the seal has been made and before the thermal energy employed to form the heat seal has dissipated. The hot tack has been determined using the same Packforsk instrument. The heat seal is
15 made as described above, but just after the opening of the sealing jaws, a peeling action is automatically started and the the force to break the seal is automatically recorded and expressed as the hot tack in N/15 mm. The peeling operation
20 takes place at a controlled delay time (= time between opening of the jaws and start of the peeling operation) and controlled peel rate. The following constant conditions have been used for all hot tack determinations: delay time = 0.6
25 seconds, peel rate = 100 mm/s.

One liter empty pouches were manufactured by heat sealing films 1 and 2 to themselves. The heat seal machine was of type Transwrap, manufactured by Robert Bosch. Different seal temperature and time

settings were established to optimize pouch quality:

Film 1 Dwell time - 1.6 sec. - seal temperature
175° Centigrade.

5 Film 2 Dwell time - 1.2 sec. - seal temperature
175° Centigrade.

The shorter dwell time with Film 2 is made possible by the better hot tack of Film 2 (see Table 3 and Figure 2).

10 The pouches were filled with one liter of demineralized water, and bottom and top sealed on a Brugger Impulse Sealer with the same settings:

Dwell time - 1.5 seconds, seal pressure : one bar.

15 Impulse seal current - 2x61 amps.

They were then sterilized in a Getinge Autoclave Type GE-306 EC1 using a direct water spray and 25 minute exposure to 121°C. The air counter-pressure used in the autoclave was 2.5 bars and cooling was
20 carried out with 40°C water.

The filled and sterilized one liter pouches were submitted to various abuse testing - similar to those used in the intravenous solution industry : drop impact resistance, burst resistance and
25 microscopy investigation.

The accompanying Table 4 summarizes the drop impact and burst resistance of the pouches made out of Films 1 and 2.

Microscopic evaluation indicates that Film 2 seal edges are round while Film 1 seal edges have a much sharper shape. This difference is visible in the sterilized pouches that had not been dropped ("ST"), the sterilized pouches that had been dropped without failure ("ST. DR.") and in the sterilized pouches that had failed the drop test ("ST. DR. F.").

These tests were carried out under the following conditions:

Drop Impact Resistance

One hundred one liter pouches were dropped from a horizontal position from a height of 2 meters on a smooth cement surface. They were then inspected for leaks by manually squeezing them.

Burst Resistance by Pressure Cuff

Individual pouches were compressed in a commercial pressure cuff Type C-Fusor 1000 sold by Medex Inc. used for pressure infusion of intravenous (IV) solutions in emergency situations. The pressure applied was 400 mm Hg during 15 minutes.

Thimonnier Burst Tester

5 This consists essentially of a plexiglass box with a piston-driven upper part. A filled pouch is introduced by opening a lateral side of the box. The piston then moves the upper part downward at a constant pressure (7 bars). The pouch is being pressed during 30 minutes after which it is inspected for leaks and deformation.

10 Microscopy Evaluation of the Seal Edge

Filled and sterilized pouches were emptied and the side seals were cut and their edges were examined with a microscope (type Wild) equipped with a photographic head.

15 Results

Table 1 shows that Film 2 is tougher than Film 1 (higher tensile at yield and at break). This result is obtained without compromising film softness (as measured by the 1% secant modulus).

20 Table 2 illustrates the higher clarity of Film 2 (lower haze), and also the lower moisture barrier which is the result of the more amorphous nature of the polypropylene.

25 Table 3 (and Figures 1 and 2) shows the superior seal strength of Film 2, which can be related to higher toughness, and also the superior "hot tack"

of Film 2 in the 120°C-150°C range, which suggests that Film 2 may run faster on form/fill/seal (FFS) packaging machines.

Table 4 outlines the very significantly improved drop resistance of Film 2 after sterilization; also microscopy pictures indicate the very distinct shapes of the seal edge obtained: Film 2 seal edges have a round shape while Film 1 are sharp. It is well known that sealed pouches with a wide radius at the seal edge allow a distribution on a wider film surface of the stress created by the impact of a pouch dropped from 2 meters high, and therefore are more impact resistant.

It is quite surprising to find out that the use of a high ethylene content in the random copolypropylene has such a positive effect on the film physical characteristics and the pouch impact resistance, compared to prior art polypropylene copolymer films based on a lower ethylene content.

TABLE 1
MECHANICAL PROPERTIES

	<u>FILM 2</u>		<u>FILM 1</u>	
	ORIGINAL	STERILIZED	ORIGINAL	STERILIZED
<hr/>				
MD				
TENSILE (MPa)				
at yield	14.6	18.1	9.9	11.5
at break	31.8	33.8	20.7	19.3
ELONGATION (%)				
at yield	26	24	11	25
at break	578	614	589	558
SECANT MODULUS	214	256	259	244
1 $\frac{1}{2}$ (MPa)				
<hr/>				
TD				
TENSILE (MPa)				
at yield	13.3	17	7.3	11.9
at break	32.2	30.7	16.7	20.8
ELONGATION (%)				
at yield	25	24	13	24
at break	695	601	595	590
SECANT MODULUS	198	242	190	260
1 $\frac{1}{2}$ (MPa)				

TABLE 2

OPTICAL & BARRIER PROPERTIES

	<u>FILM 2</u>		<u>FILM 1</u>	
	ORIGINAL	STERILIZED	ORIGINAL	STERILIZED
HAZE, AIR	6.1	17.3	21.2	18.3
WVTR (g/m ² day)	3.2	3.2	1.7	1.7

TABLE 3

SEALABILITY: COLD SEAL STRENGTH AND HOT TACK

FILM 1										
USA PATENT # 4,857,409										
TEMP (°C)	HOT TACK N/15mm	HEAT SEAL				HOT TACK N/15mm	HEAT SEAL			
		STRENGTH		ELONGATION %	PEELING %		STRENGTH		ELONGATION %	PEELING %
		N/15mm	MPa				N/15mm	MPa		
100	NO SEAL	---	---	---	---	NO SEAL	---	---	---	
110	NO SEAL	---	---	---	---	NO SEAL	---	---	---	
120	1.4	0	0	0	---	0.4	0	0	---	
130	3.6	18.5	6	21	100	1.1	0	0	---	
140	3.0	39.6	13	144	30	2.6	24.4	9	100	
150	3.0	41.0	14	307	0	2.8	32.9	12	50	
160	2.1	45.9	15	306	0	2.3	32.8	12	0	
170	2.2	46.4	15	332	0	2.1	30.4	11	0	
180	2.1	46.1	15	339	0	1.7	33.5	12	0	
190	1.7	49.2	16	367	0	1.6	33.8	12	0	
200	1.4	50.2	17	372	0	1.4	33.1	12	0	

TABLE 4DROP IMPACT AND BURST RESISTANCE OF STERILIZED POUCHES

	FILM 2	FILM 1 AS PER USA PATENT #4857409
DROP IMPACT		
% SEAL FAILURES	4	38
BURST RESISTANCE		BALLOONING AND BURSTING
BY PRESSURE CUFF	NO FRACTURE	AT 350 MM Hg
THIMONNIER BURST	NO FRACTURE AT 7	BALLOONS AND EXPLODES
TESTER	BARS* DURING 15 MINUTES	AT 7 BARS*

* 7 bars at the piston corresponds to 0.12 bars on the bag.

It should be understood that the present invention applies to pouches or containers formed from monolayers of isotactic random reactant copolymers of polypropylene and from about 5% to about 20% by weight of ethylene, sealed to each other, or to pouches or containers formed from multilayer laminates or coextrudates of such copolymer films and other films such as polyolefins, black copolymer films, etc., provided that the high ethylene random copolymer film is the surface film which is heat-sealed to itself to form the pouch or container.

Among the preferred high ethylene random copolymer films for use according to the present invention are Exxon films PLTD 661, 6.1% ethylene, MPt 122.5°C, remelt temp. 124.9°C, and PLTD 572-2, 6.7% ethylene, MP+ 116.9°C, remelt temp. 121.9°C.

It will apparent to those skilled in the art in the light of the present disclosure, that other pure random polymers of polypropylene and from about 5 to 20% by weight of ethylene, most preferably from about 5.5 to 10% by weight of ethylene, are also suitable for use according to the present invention, including terpolymers containing minor amounts, up to about 5% by weight of other olefinic monomers containing from 4 to 8 carbon atoms, such as butene, provided that they have remelt temperatures, preferably below about 125°C and above about 120°C so as to reform their heat seals under normal steam sterilization temperatures.

It is to be understood that the above described embodiments of the invention are illustrative only and that modifications throughout may occur to those skilled in the art. Accordingly, this invention is not to be regarded as limited to the embodiments disclosed herein but is to be limited as defined by the appended claims.

CLAIMS

1. Process for producing heat-sealable containers or pouches of plastic film, which are heat-sterilizable at temperatures between about 120°C and 130°C and which reform their heat seals at such temperatures in order to retain the flexibility and resistance of said heat seals to rupture or leak under impact and/or compression forces, comprising forming said pouches or containers by superposing films of isotactic random reactant polymers of polypropylene containing from about 5% to about 20% by weight of ethylene, heat sealing said films to each other to form containers or pouches on which the heat-seals remelt and reform during heat-sterilization of the container or pouch at a temperature within the range of from about 120°C to about 130°C.

2. Process according to claim 1 in which said films of isotactic random reactant polymers are monofilms.

3. Process according to claim 1 in which said films of isotactic random reactant polymers comprise the surface films of multi-film laminates, which surface films are heat-sealed to each other.

4. Process according to claim 1 in which said films of isotactic random reactant polymers have a thickness between about 6 and 10 mils.

5. Process according to claim 1 in which said films of isotactic random reactant polymers contain from about 5.5% to 10% by weight of polyethylene.

6. Process according to claim 1 in which said films of isotactic random reactant polymers provide heat seals which remelt and reform at a temperature of 125°C or less.

7. A heat-sealable container or pouch of plastic film, which is heat-sterilizable at temperatures between about 120°C and 130°C and which reforms its heat seals at such temperatures in order to retain the flexibility and resistance of said heat seals to rupture or leak under impact and/or compression forces, comprising superposed films of isotactic random reactant polymers of polypropylene containing from about 5% to about 20% by weight of ethylene which are heat-sealed to each other to form a container or pouch, the heat seals between said films being remeltable and reformable during sterilization within the range of from about 120°C to 130°C to render the container or pouch resistant to rupture or leakage under impact and/or compressive forces.

8. A container or pouch according to claim 7 in which said films of isotactic random reactant polymer are monofilms.

9. A container or pouch according to claim 7 in which said films of isotactic random reactant

polymer comprise the surface films of multi-film laminates, which surface films are heat-sealed to each other.

10. A container or pouch according to claim 7 in which said films of isotactic random reactant polymers have a thickness between about 6 and 10 mils.

11. A container or pouch according to claim 7 in which said films of isotactic random reactant polymers contain from about 5.5% to 10% by weight of polyethylene.

12. A container or pouch according to claim 7 in which said films of isotactic random reactant polymers provide heat seals which remelt and reform at a temperature of 125°C or less.

13. A container or pouch according to claim 7 having a capacity of one liter or more.

HEAT SEAL STRENGTH

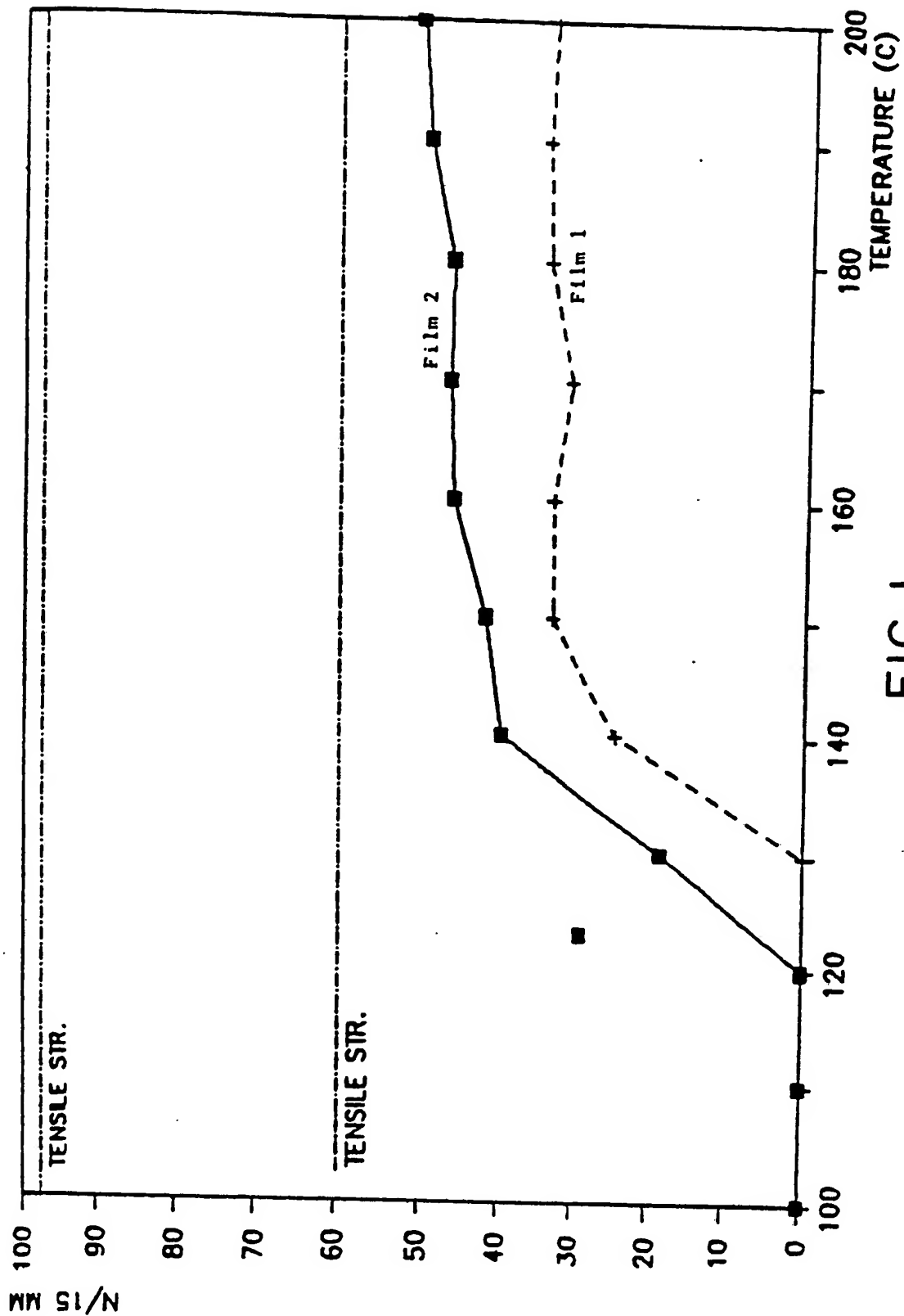


FIG. I

HOT TACK

PACKFORSK

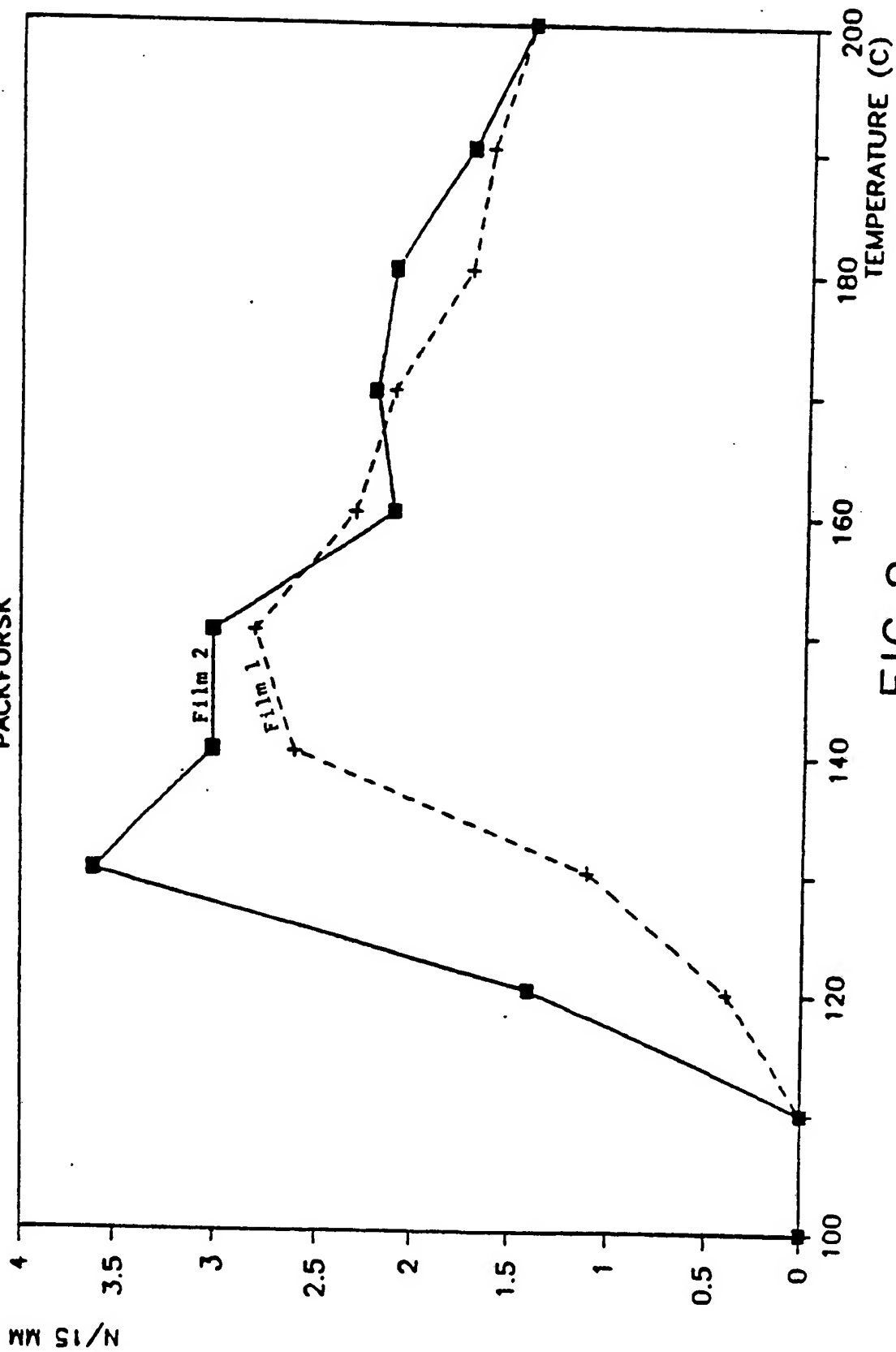


FIG. 2

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C09J123/16; C08L23/16		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C09J ; C08L ; C09D	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	DATABASE WPIL Section Ch, Week 8521, Derwent Publications Ltd., London, GB; Class A96, AN 85-125222 & JP,A,60 063 059 (DAINIPPON PRINTING) 11 April 1985 see abstract	1-12
X	EP,A,0 061 238 (IMPERIAL CHEMICAL INDUSTRIES) 29 September 1982 see claims 1-10	1,3-7, 9-12
X	EP,A,0 333 973 (ALKOR GMBH KUNSTSTOFFE) 27 September 1989 see claims 1,4	1,3-7, 9-12

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¹⁰ Special categories of cited documents : ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "A" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search 23 JULY 1993		Date of Mailing of this International Search Report 09.08.93
International Searching Authority EUROPEAN PATENT OFFICE		Signature of Authorized Officer GOOVAERTS R.E.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category ^a	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claims No.
X	<p>DATABASE WPI Section Ch, Week 7743, Derwent Publications Ltd., London, GB; Class A92, AN 77-76865 & JP,A,52 110 783 (DAINIPPON PRINTING) 17 September 1977 see abstract</p> <p>-----</p>	<p>1,3-7, 9-12</p>

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9301812
SA 71364

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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